Supplementary Material

Table S1. Experimental design for imidacloprid and thiamethoxam study.

Treatment	Photocycle	Sampling Frequency
NP NP +NaN_3 NP+IPA NP+TEMPOL Mis DOM Mis DOM+NaN_3 Mis DOM+IPA Mis DOM+TEMPOL Suw DOM Suw DOM+NaN_3 Suw DOM+IPA Suw DOM+TEMPOL	0-12h 12 hrs Static Light (650 W m^{-2}) 12-24 h 2. 12 hrs Dark 24-36 h 12 hrs Static Light (650 W m^{-2})	0, 1, 4, 8, 12, 18, 24, 28, 32, and 36 h

* *"NP" represents nanopure water, "Mis DOM" represents Mississippi River DOM, and "Suw DOM" represents Suwannee River DOM*

Table S2. Parameters for LC-MS/MS Analysis

Compound	Parent-Daughter m/z	Cone (V)	Collision (V)	Retention Time (min)
Clothianidin-d3 (IS)	252.968>171.922	34	12	1.70
	252.968>131.914	34	14	
Imidacloprid-d4 (IS)	260.032>179.059	40	16	1.70
	260.032>213.138	40	12	
Metalaxyl-d6 (IS)	286.16>226.141	36	12	2.67
	286.16>44.94	36	32	
Pyraclostrobin-d3 (IS)	391.096>197.069	44	10	3.25
	391.096>162.99	44	24	
Thiamethoxam-d3 (IS)	294.968>213.938	28	10	1.47
	294.968>183.951	28	22	
Nitenpyram (Sur)	271.032>55.997	28	28	1.29
	271.032>98.93	28	14	
Terbuthylazine (Sur)	230.096>173.948	38	14	2.89
	230.096>95.946	38	26	
Dimoxystrobin (Sur)	327.096>205.056	2	8	3.15
	327.096>115.96	2	22	
Acetamiprid	223.032>125.92	62	18	1.85
	223.032>55.996	62	14	
Clothianidin	249.968>168.86	34	10	1.70
	249.968>131.908	34	12	
Dimethoate	229.968>198.864	26	8	1.81
	229.968>124.896	26	20	

Compound	Parent-Daughter m/z	Cone (V)	Collision (V)	Retention Time (min)
Dinotefuran	203.096>129.052	20	10	1.13
	203.096>86.965	20	14	
Imidacloprid	256.032>174.982	32	18	1.70
	256.032>209.066	32	14	
Metalaxyl	280.096>220.08	32	12	2.68
	280.096>44.94	32	28	
Thiacloprid	253.032>125.929	54	22	1.99
	253.032>90.02	54	34	
Thiamethoxam	291.968>210.941	28	10	1.47
	291.968>180.954	28	22	
Azoxystrobin	404.032>372.014	18	12	2.83
	404.032>328.962	18	30	
Picoxystrobin	368.032>144.981	18	20	3.13
	368.032>205.013	18	6	
Pyraclostrobin	388.032>194.01	28	10	3.24
	388.032>163.114	28	24	
Trifloxystrobin	409.096>185.947	38	14	3.36
	409.096>144.972	38	46	
Sulfoxaflor	278.047>173.989	36	6	1.91*
	278.047>154.021	36	26	
Indoxacarb	528.042>149.972	38	22	3.35
	528.042>292.978	38	12	
Imidacloprid urea	213.065>127.956	78	20	1.02
	213.065>90.024	78	34	
Imidacloprid olefin	253.97>205.187	28	14	1.55
	253.97>125.978	28	26	
Imidacloprid desnitro	211.064>125.947	64	24	1.02
	211.064>90.01	64	34	
Thiamethoxam urea	248.03>174.913	54	18	1.86
	248.03>44.026	54	14	

Table S3. Water quality parameters in various water experiments in light experiments.

Experiment	NO_3-N (mg/L)	DOC (mg C/L)	pH	Br^- (mg/L)	DO (mg/L)	Cl^- (mg/L)	PO_4^{3-}-P (mg/L)	Specific Conductivity (µS/cm)
NP	10.0	47.6	6.10	<0.01	6.90	<0.01	<0.01	52.3
NP + NaN_3	43.5	50.1	6.87	<0.01	6.48	<0.01	<0.01	718
NP+IPA	6.03	38.7	7.01	<0.01	6.18	0.06	<0.01	29.7
NP+TEMPOL	8.92	37.2	7.78	<0.01	6.87	0.019	<0.01	85.2
MIS DOM	9.58	48.2	6.54	<0.01	4.28	0.037	0.447	57.1
MIS DOM+ NaN_3	29.5	49.0	6.08	<0.01	6.46	<0.01	<0.01	398
MIS DOM+IPA	9.54	62.8	5.71	<0.01	6.61	0.034	0.472	51.2
MIS DOM +TEMPOL	--	---	7.32	<0.01	4.04	--	---	---
SUW DOM	9.70	38.3	6.94	<0.01	5.88	0.043	<0.01	54.6
SUW DOM + NaN_3	51.9	52.7	6.22	<0.01	6.90	<0.01	<0.01	815
SUW DOM +IPA	10.5	49.5	4.99	<0.01	6.65	0.082	0.453	69.6
SUW DOM +TEMPOL	9.52	43.5	6.53	<0.01	5.94	0.097	0.227	54.5
Detection Limit	**0.10**	**0.05**	-	**0.10**	**-**	**0.10**	**0.10**	**0.10**

Table S4. Significance grouping for MIS DOM photodegradation concentration by time (h)

Time (h)	Imidacloprid	Thiamethoxam
0	A	A
1	A	A
4	AB	AB
8	BC	BC
12	CD	CD
18	CDE	CD
24	DE	CD
28	DEF	DE
32	EF	EF
36	F	F

Table S5. Significance grouping for MIS DOM photodegradation concentration by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid	Thiamethoxam
MIS CONTROL	B	B
MIS TEMPOL	A	A
MIS IPA	C	C
MIS NaN3	C	B

Table S6. Significance grouping for MIS DOM photodegradation removal rate by time (h)

Time (h)	Imidacloprid	Thiamethoxam
0	A	A
1	A	A
4	A	A
8	A	A
12	AB	A
18	BC	AB
24	BC	A
28	BC	AB
32	C	A
36	C	B

Table S7. Significance grouping for MIS DOM photodegradation removal rate by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid	Thiamethoxam
MIS CONTROL	C	B
MIS TEMPOL	C	B
MIS IPA	B	A
MIS NaN3	A	A

Table S8. Significance grouping for SUW DOM photodegradation concentration by time (h)

Time (h)	Imidacloprid	Thiamethoxam
0	A	A
1	B	A
4	C	B
8	D	C
12	E	D
18	EF	D
24	F	D
28	G	E
32	G	F
36	G	F

Table S9. Significance grouping for SUW DOM photodegradation concentration by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid	Thiamethoxam
SUW CONTROL	AB	B
SUW TEMPOL	A	AB
SUW IPA	B	AB
SUW NaN3	B	A

Table S10. Significance grouping for SUW DOM photodegradation removal rate by time (h)

Time (h)	Imidacloprid	Thiamethoxam
0	A	A
1	A	A
4	A	A
8	A	A
12	B	B
18	C	BC
24	C	BC
28	D	BC
32	D	C
36	D	D

Table S11. Significance grouping for SUW DOM photodegradation removal rate by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid	Thiamethoxam
SUW CONTROL	B	B
SUW TEMPOL	C	C
SUW IPA	A	A
SUW NaN3	AB	AB

Table S12. Significance grouping for NP photodegradation concentration by time (h)

Time (h)	Imidacloprid	Thiamethoxam
0	A	A
1	A	A
4	B	B
8	C	C
12	DE	D
18	D	D
24	DE	D
28	DE	E
32	E	F
36	E	F

Table S13. Significance grouping for NP photodegradation concentration by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid	Thiamethoxam
NP CONTROL	B	B
NP TEMPOL	AB	A
NP IPA	A	A
NP NaN3	AB	A

Table S14. Significance grouping for NP photodegradation removal rate by time (h)

Time (h)	Imidacloprid	Thiamethoxam
0	AB	A
1	A	A
4	A	A
8	BC	A
12	C	B
18	D	B
24	D	B
28	D	B
32	D	C
36	D	C

Table S15. Significance grouping for NP photodegradation removal rate by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid	Thiamethoxam
NP CONTROL	AB	A
NP TEMPOL	BC	B
NP IPA	A	A
NP NaN3	C	AB

Table S16. Effects of isopropanol, NaN_3, and TEMPOL on the photodegradation kinetics of imidacloprid and thiamethoxam in simulated Mississippi DOM

MIS DOM			Imidacloprid		Thiamethoxam	
Photocatalytic Condition	*Quenching RS Species*	*Quencher Concentration (Mm)*	*K (1/h)*	*R (%)*	*K (1/h)*	*R (%)*
No scavengers	-	10	0.296	-	0.203	-
NaN_3	$^1O_2$ and $^{\bullet}OH$	10	0.485	0.0%	0.251	5.6%
TEMPOL	$O_2^{\bullet-}$	10	0.156	63.0%	0.027	72.2%
IPA	$^{\bullet}OH$	10	0.515	0.0%	0.291	0.0%

Table S17. Effects of isopropanol, NaN_3, and TEMPOL on the photodegradation kinetics of imidacloprid and thiamethoxam in simulated Suwanee DOM

SUW DOM			Imidacloprid		Thiamethoxam	
Photocatalytic Condition	*Quenching RS Species*	*Quencher Concentration (Mm)*	*K (1/h)*	*R (%)*	*K (1/h)*	*R (%)*
No scavengers	-	10	0.372	-	0.230	-
NaN_3	$^1O_2$ and $^{\bullet}OH$	10	0.437	0.6%	0.218	6.5%
TEMPOL	$O_2^{\bullet-}$	10	0.380	13.0%	0.225	5.3%
IPA	$^{\bullet}OH$	10	0.465	0.0%	0.250	0.0%

Table S18. Effects of isopropanol, NaN_3, and TEMPOL on the photodegradation kinetics of imidacloprid and thiamethoxam in simulated Nanopure water

Nanopure			Imidacloprid		Thiamethoxam	
Photocatalytic Condition	*Quenching RS Species*	*Quencher Concentration (Mm)*	*K (1/h)*	*R (%)*	*K (1/h)*	*R (%)*
No scavengers	-	10	0.531	-	0.340	-
NaN_3	$^1O_2$ and $^{\bullet}OH$	10	0.587	16.8%	0.312	0.0%
TEMPOL	$O_2^{\bullet-}$	10	0.543	0.0%	0.274	12.0%
IPA	$^{\bullet}OH$	10	0.623	0.4%	0.397	11.4%

Table S19: Significance grouping for MIS DOM byproduct concentration by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid urea	Imidacloprid desnitro	Thiamethoxam urea
MIS CONTROL	A	A	C
MIS TEMPOL	A	A	B
MIS IPA	B	B	A
MIS NaN_3	B	B	AB

Table S20: Significance grouping for SUW DOM byproduct concentration by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid urea	Imidacloprid desnitro	Thiamethoxam urea
SUW CONTROL	A	A	B
SUW TEMPOL	A	A	A
SUW IPA	B	B	A
SUW NaN3	A	AB	B

Table S21: Significance grouping for Nanopure byproduct concentration by treatment (e.g., TEMPOL, NaN_3, and IPA)

Treatment	Imidacloprid urea	Imidacloprid desnitro	Thiamethoxam urea
NP CONTROL	A	A	A
NP TEMPOL	A	A	A
NP IPA	B	B	B
NP NaN3	B	B	A

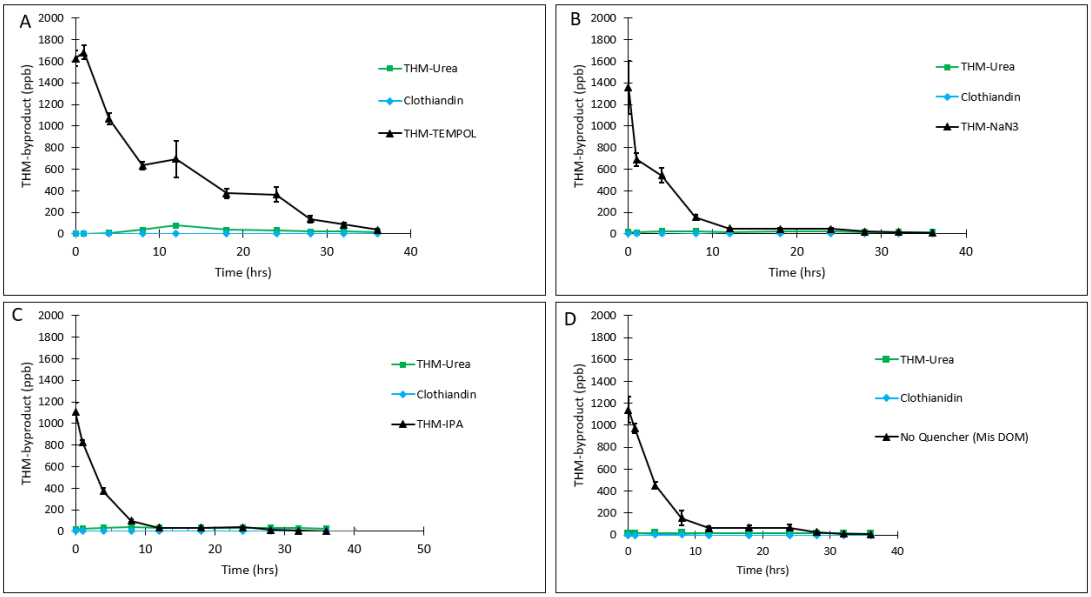

Figure S1 Phototransformation of parent and byproducts formed in Mississippi river DOM under simulated light for A) thiamethoxam with TEMPOL (n=3)., B) thiamethoxam with NaN_3 (n=3), C) thiamethoxam with IPA (n=3), and D) thiamethoxam without scavenging agents (n=9)

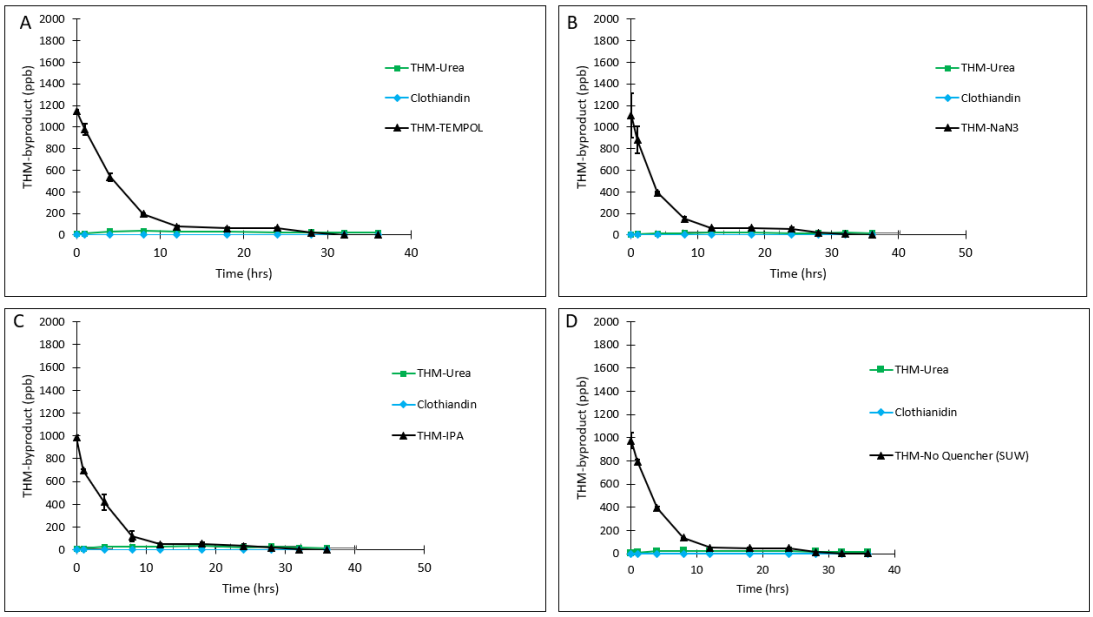

Figure S2. Phototransformation of parent and byproducts formed in Suwannee River DOM under simulated light for A) thiamethoxam with TEMPOL (n=3)., B) thiamethoxam with NaN_3 (n=3), C) thiamethoxam with IPA (n=3), and D) thiamethoxam without scavenging agents (n=9)

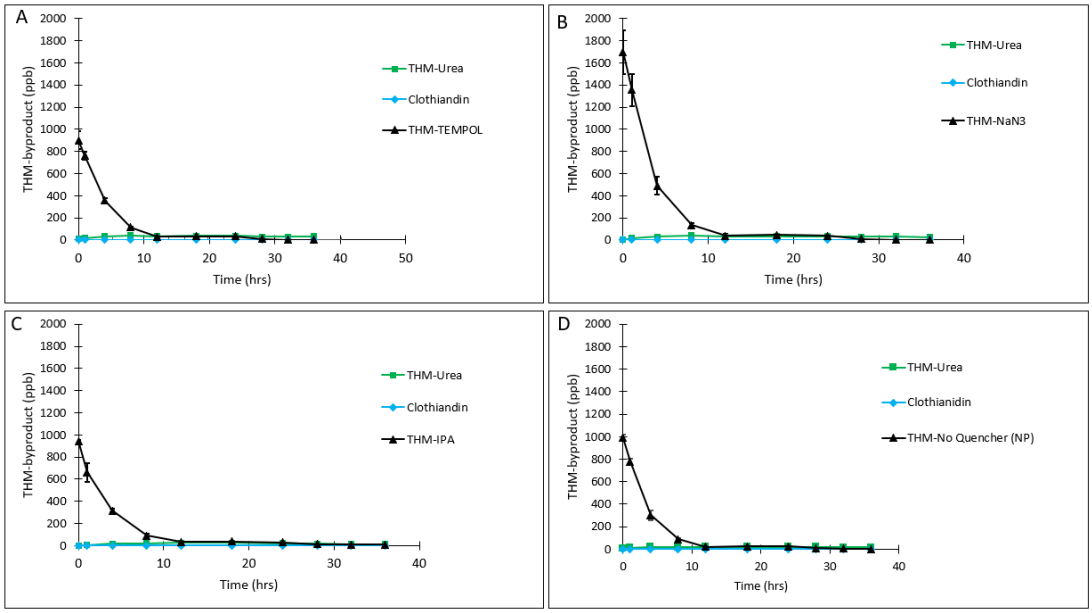

Figure S3. Phototransformation of parent and byproducts formed in Nanopure water under simulated light for A) thiamethoxam with TEMPOL (n=3)., B) thiamethoxam with NaN3 (n=3), C) thiamethoxam with IPA (n=3), and D) thiamethoxam without scavenging agents (n=9)

Equations

Equation S1:

$$\ln\frac{C(t)}{C(0)} = -kt \quad \text{(S1)}$$

where, C (0) was the analyte concentration at the initiation of the experiments (μg/L), C(t) was the analyte concentration at end of the experiments (μg/L), t was the experiment time (h), and k was the first order removal rate constant (h).

Equations S2-S5:

$$R_{\cdot OH} = \frac{k_{\cdot OH}}{k} * 100 = \frac{k - k_{isopropanol}}{k} * 100\% \quad \text{(S2)}$$

$$R_{^1O_2} = \frac{k^1O_2}{k} * 100 = \frac{k_{isopropanol} - k_{NaN3}}{k} * 100\% \quad \text{(S3)}$$

$$R_{O_2^{\cdot-}} = \frac{k_{O_2^{\cdot-}}}{k} * 100 = \frac{k - k_{TEMPOL}}{k} * 100\% \quad \text{(S4)}$$

$$R_{direct} = 100\% - R_{\cdot OH} - R_{^1O_2} - R_{O_2^{\cdot-}} \quad \text{(S5)}$$

where *R* values were the contribution rate of ROS, $k_{isopropanol}$, k_{NaN3}, and k_{TEMPOL} were the parent rate constants for the addition of isopropanol, sodium azide, and TEMPOL, and *k* was the rate constant of parent photolysis without the addition of isopropanol, NaN_3, or TEMPOL.

Equations S6-S12

$$IMI/THM \xrightarrow{h\nu} {}^3IMI/THM^* \rightarrow products \quad \text{S6}$$

$${}^3IMI/THM^* + O_2 \rightarrow IMI/THM + {}^1O_2 \quad \text{S7}$$

$${}^3IMI/THM^* + O_2 \rightarrow IMI/THM + {}^1O_2 \quad \text{S8}$$

$${}^3IMI/THM^* + O_2 \rightarrow IMI/THM + O_2^{\cdot-} \quad \text{S9}$$

$${}^3IMI/THM^* + O_2 \rightarrow IMI/THM + O_2^{\cdot-} \quad \text{S10}$$

$$O_2^{\cdot-} + H^+ \rightarrow .O_2H \rightarrow H_2O_2 \rightarrow .OH \quad \text{S11}$$

$$O_2^{\cdot-}/{}^1O_2 / OH + IMI/THM \rightarrow products \quad \text{S12}$$